

Figure 3. Traces of single molecules of **1** diffusing through a 2.8 fL (10^{-15} L) fluorescence element. a) Single molecules are readily detected in *n*-heptane solution in an argon or nitrogen atmosphere. b) Transients from these molecules disappear as the atmosphere is changed to carbon dioxide and c) reappear upon returning to an argon or nitrogen atmosphere.

those from **2**. While both materials share comparable spectroscopic properties and solvent sensitivity, the number of single molecule events was decreased but not eliminated when **2** was subjected to the same conditions as those used in Figures 2 and 3.

The fluorescence observed from the switching of **1** was translated into a graphical display (Figure 3) by conversion of the fluorescent photons into an electrical signal by means of a single-photon counting photoavalanche detector. The relay of the interaction between atmosphere and molecular photo-physics to an electrical signal provides a novel approach for the design of future optical mechanical and electronic devices.

Experimental Section

Measurements were conducted on a conventional confocal single molecule spectrometer.^{16, 71} A 20 μ L drop of water was placed on the upper side of a circular cover-slip (Fischer) and attached to the head of a microscope objective (Zeiss Plan-neofluar Multi-immersion 40X). A 50 μ L gold well encased in a silver holder ($2 \times 2 \times 0.6$ cm) and loaded with 80 ± 10 μ L of a 100 pM solution of **1** in benzene or toluene was slowly brought into contact with the cover-slip. The assembly was held in place by mounting the sample holder on to the objective with four beams (see Figure 2). The droplet of **1** was open to the atmosphere. A balloon was placed over the entire sample housing and filled with gas. Confocal single molecule examinations were made repetitively on solutions of **1** in argon, nitrogen, and carbon dioxide atmospheres.

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- [7] Single molecules were detected using a confocal fluorescence spectrometer as designed by Eigen–Rigler.^[6a,b] Fluorescent photons were harvested by passing the filtered fluorescent beam through a 1 μ m diameter pinhole and focusing this light on to a single photon counting silicon avalanche detector (EG&G SPCM-100).
- [8] The switch was flipped by changing the atmosphere within the balloon between argon or nitrogen and carbon dioxide. This was conveniently accomplished by slowly purging and filling with the appropriate gas.
- [9] The fact that the regenerated signal (Figure 3, bottom trace) originated from **1** was verified by two observations. Firstly, the detected transients displayed an identical diffusion time ($t_d = 55 \pm 5$ ms) with that of **1**, as given by their auto-correlated function (not shown). Secondly, the reaction of **1** with carbon dioxide was reversible as indicated by independent ¹H NMR characterization of a scaled-up version of this process.

Novel Catalytic Hydrogenolysis of Trimethylsilyl Enol Ethers by the Use of an Acidic Ruthenium Dihydrogen Complex**

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Since the first report on a tungsten complex with an η^2 -bound H_2 ligand, $W(\eta^2-H_2)$, by Kubas and co-workers in 1984,^[1] a great number of this unique class of complexes have

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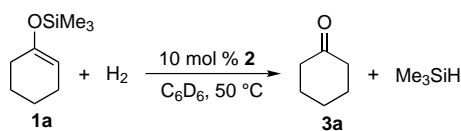
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been found and their structures and reactivities have been delineated.^[2, 3] Dihydrogen complexes allow the design of a simple fascinating pathway for the heterolytic activation of molecular dihydrogen (H₂) on a transition metal center. Actually, the heterolytic cleavage of coordinated H₂ has been achieved by treatment with a variety of bases.^[2, 3] This has led to systematic investigation of ligand effects on the reactivity of coordinated H₂ and to the synthesis of highly acidic M(η^2 -H₂) complexes.^[2, 3] However, the catalytic reactions that proceed through heterolytic activation of H₂ by acidic M(η^2 -H₂) complexes are limited.^[3f, 4-7] Very recently, we have succeeded in the formation of NH₃ by the protonation of the coordinated N₂ on a tungsten atom with an acidic Ru(η^2 -H₂) complex under mild conditions.^[8] This finding has led us to develop a novel catalytic reaction in which the heterolytic activation of H₂ is catalyzed by an acidic Ru(η^2 -H₂) complex.

Transition metal catalyzed hydrogenation of a variety of unsaturated substrates is an important and conventional method in preparative organic chemistry.^[9] The Wilkinson complex, [RhCl(PPh₃)₃], is probably one of the most widely used catalysts for the homogeneous hydrogenation of carbon–carbon double bonds in the laboratory.^[9] For example, trimethylsilyl enol ethers are converted into saturated trimethylsilyl ethers in the presence of [RhCl(PPh₃)₃] under an atmospheric pressure of H₂.^[10, 11] In this case, the addition of H₂ to the carbon–carbon double bond occurs. In sharp contrast to the conventional hydrogenation, we have now found that employment of an acidic Ru(η^2 -H₂) complex as catalyst results in hydrogenolysis of the Si–O bond. In this reaction, H₂ is heterolytically cleaved into H⁺ and H[−] on the Ru center and transferred to the enol oxygen^[12] and the trimethylsilyl silicon atom, respectively, affording a ketone and Me₃SiH. This provides a conceptually new type of catalytic reaction. Preliminary results on this catalytic reaction are described here.

Treatment of 1-trimethylsilyloxy-1-cyclohexene (**1a**) in the presence of a catalytic amount of [RuCl(dppe)₂]OTf (**2**) (10 mol %) (dppe = 1,2-bis(diphenylphosphanyl)ethane, Tf = trifluoromethanesulfonyl) under 1 atm of H₂ in anhydrous C₆D₆ at 50 °C for 3 h in an NMR tube afforded cyclohexanone (**3a**) and Me₃SiH in almost quantitative yields by NMR spectroscopy (Scheme 1). This novel reaction proceeded

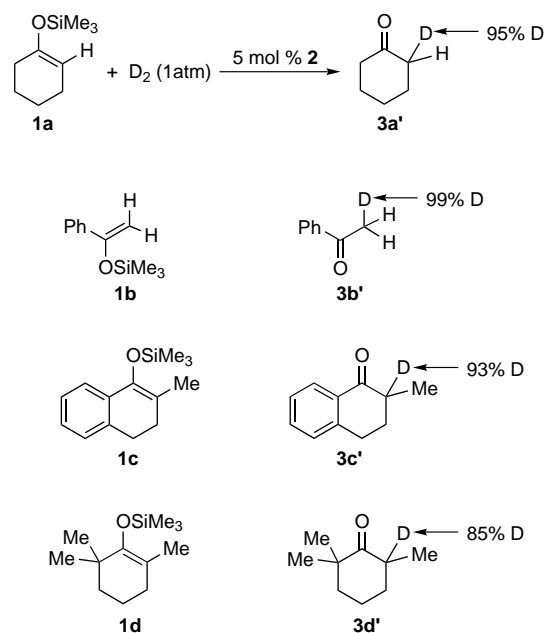


Scheme 1. Hydrogenolysis of **1a** into **3a** and Me₃SiH. ²⁹Si{¹H} NMR of **1a** (C₆D₆): $\delta = 14.6$; ²⁹Si{¹H} NMR of Me₃SiH (C₆D₆): $\delta = -16.4$.

smoothly at 50 °C, however, very slowly at room temperature. The formation of Me₃SiH was confirmed by the ¹H and ²⁹Si{¹H} NMR spectra of the reaction mixture. No other products were observed by NMR spectroscopy, gas–liquid chromatography (GLC), and gas chromatography mass spectrometry (GC-MS). Under 1 atm of H₂, complex **2** was quantitatively converted into [RuCl(η^2 -H₂)(dppe)₂]OTf (**4**) within 5 min at ambient temperature. Since complex **4** has

relatively high acidity,^[14] **1a** is considered to be protonated at the oxygen atom by the coordinated H₂ in **4** to give **3a**, while the Me₃Si group in **1a** eventually binds with the remaining hydride to form Me₃SiH (vide infra). Interestingly, the reaction between **1a** and [RuH(η^2 -H₂)(dppe)₂]OTf with low acidity^[15] did not occur.

The direct proton transfer from H₂ to **1a** catalyzed by complex **2** was confirmed by the experiment employing D₂ gas. The reaction of **1a** was carried out under 1 atm of D₂ at 50 °C for 48 h in the presence of 5 mol % of **2** in anhydrous dichloroethane. This reaction resulted in **3a'** in >95 % yield (GLC) with monodeuteration at the α -position (Scheme 2).



Scheme 2. Hydrogenolysis of **1a–d** with D₂.

Other trimethylsilyl enol ethers (**1b–d**) were also protonated with D₂ to give ketones (**3b'–d'**) in >95 % yields (GLC) with monodeuteration at the α -position. Incorporation of D at the α -position of **3a'–d'** was quantitatively analyzed by ¹H NMR spectroscopy and GC-MS (see Scheme 2 and Supporting Information for experimental details). These results indicate that one of the deuterium atoms of the coordinated D₂ is catalytically transferred to the oxygen atom, and the resultant enol then tautomerizes to form the corresponding ketone with monodeuteration at the α -position. When THF or benzene was used as solvent in place of dichloroethane, almost the same results were obtained.

By contrast, the catalytic hydrogenation of trimethylsilyl enol ethers using [RhCl(PPh₃)₃] under the same reaction conditions led to the formation of the corresponding trimethylsilyl ethers. For example, treatment of **1b** in the presence of 5 mol % of [RhCl(PPh₃)₃] under 1 atm of H₂ in anhydrous C₆H₆ at 50 °C for 24 h afforded (1-phenyl-1-trimethylsilyloxy)ethane in >95 % yield (GLC).

Figure 1 shows the unequivocal effect of H₂ on the conversion of **1a** into **3a** catalyzed by complex **2**. Under 1 atm of N₂ the reaction of **1a** in the presence of 1 mol % of **2**

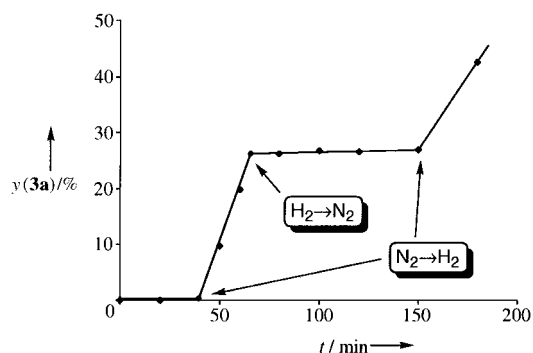
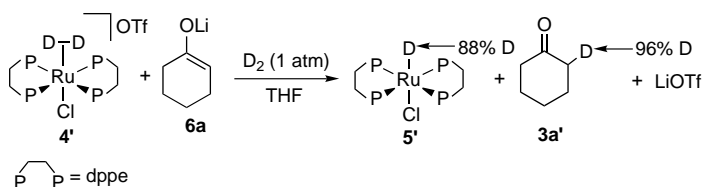


Figure 1. Effect of the reaction atmosphere on the conversion of **1a** into **3a**. *y* = yield.

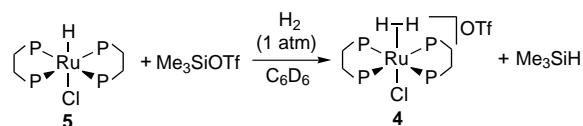
in THF at 50 °C did not occur at all. When the N₂ atmosphere was replaced by 1 atm of H₂ after 45 min, the reaction began and **3a** was rapidly produced. However, the reaction was again stopped after 60 min when the reaction atmosphere was changed back to 1 atm of N₂. Further production of **3a** started when the N₂ atmosphere was again replaced by 1 atm of H₂ after 150 min. This result demonstrates that H₂ is essential to this catalytic reaction.

To elucidate the mechanism of this novel catalytic reaction, the following stoichiometric and catalytic reactions were investigated. First, treatment of lithium enolate **6a**, which was prepared from **1a** and MeLi, with one equivalent of [RuCl(η²-D₂)(dppe)₂](OTf) (**4'**) under 1 atm of D₂ in anhydrous THF at room temperature afforded **3a'** with monodeuteration at the α-position in >95% yield (GLC) and a deuteride complex [RuClD(dppe)₂] (**5'**) in 85% yield of isolated product (Scheme 3). This provides the direct evidence of heterolytic



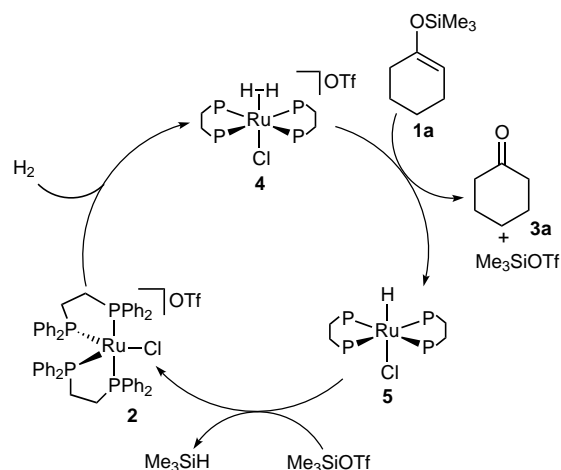
Scheme 3. Reaction between D₂ complex **4'** and lithium enolate **6a**.

cleavage of D₂ coordinated on the ruthenium atom: D⁺ is probably transferred to the sp² carbon of **6a** to form **3a'** (vide infra), while D⁻ remains at the ruthenium atom as a deuteride. Furthermore, treatment of 2-cyclohexen-1-one in the presence of a catalytic amount of **2** under 1 atm of H₂ at 50 °C did not give **3a** at all. This result indicates that the hydrogenolysis of **1a** does not proceed via 2-cyclohexen-1-one, which might be formed from dehydrosilylation of **1a**.^[16] Second, the reaction of [RuClH(dppe)₂]^[14a] (**5**) with one equivalent of Me₃SiOTf under 1 atm of H₂ in anhydrous C₆D₆ at room temperature rapidly gave **4** in quantitative NMR yield together with Me₃SiH (Scheme 4). In this stoichiometric reaction Me₃SiOTf behaves as a hydride acceptor. Thus, complex **2** may be initially formed from complex **5** by reaction with Me₃SiOTf, which is immediately converted into the starting Ru(η²-H₂) complex **4** under 1 atm of H₂.



Scheme 4. Conversion of **5** into **4**. ³¹P{¹H} NMR of **4** (C₆D₆): δ = 51.6 (s); ³¹P{¹H} NMR of **5** (C₆D₆): δ = 62.7 (s).

Based on these findings we propose a mechanism for the formation of **3a** and Me₃SiH from **1a** and H₂ (Scheme 5). The initial step is the protonation of the trimethylsilyl enol ether

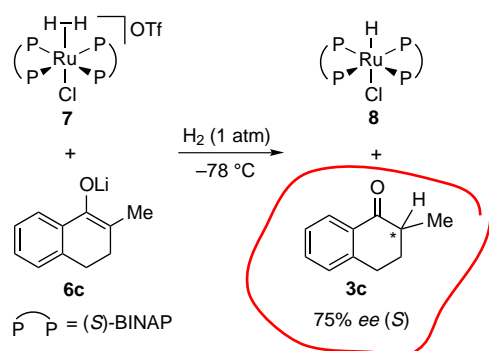


Scheme 5. A mechanism for the hydrogenolysis of **1a**.

probably at the oxygen atom with H₂ coordinated on the Ru atom; this yields **3a** and Me₃SiOTf together with **5**. Subsequent reaction of Me₃SiOTf with **5** under 1 atm of H₂ results in the formation of the starting Ru(η²-H₂) complex **4** via **2**, concurrent with Me₃SiH. We believe that a delicate balance of the acidity of the Ru(η²-H₂) complex **4** and the nucleophilicity of the hydride complex **5** might rationalize this novel hydrogenolysis.

Finally, the present hydrogenolysis has been extended to the asymmetric protonation of silyl enol ether **1c** and the corresponding lithium enolate **6c** with [RuCl(η²-H₂)((*S*)-BINAP)₂](OTf) (**7**) (BINAP = (2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl)). Treatment of **1c** with one equivalent of **7** at -78 °C in CH₂Cl₂ under 1 atm of H₂ afforded **3c** in >95% yield (GLC) with no enantioselectivity. On the other hand, the reaction of lithium enolate **6c** with 1 equiv of **7** at -78 °C in CH₂Cl₂ under 1 atm of H₂ produced **3c** with 75% *ee* (*S*) and **8**^[17] in >95% yields (Scheme 6).^[18] The enantioselective protonation of prochiral enolates has attracted much attention,^[19] thus providing a new approach to the asymmetric protonation of enol ethers. Further work on the effect of chiral ligands around the Ru atom is currently in progress.

In summary, we have found novel catalytic hydrogenolysis of trimethylsilyl enol ethers with H₂ catalyzed by [RuCl(η²-H₂)(dppe)₂](OTf) (**4**). In this reaction, the Si-O bond is heterolytically cleaved by coordinated H₂ to form a ketone and Me₃SiH. We have also demonstrated the stoichiometric, but enantioselective ruthenium-assisted protonation of a



Scheme 6. Asymmetric protonation of **6c**.

prochiral lithium enolate with H_2 to give a chiral ketone with high enantioselectivity (up to 75% ee).

Experimental Section

Preparation of $2 \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$: This complex was prepared from *cis*- $[\text{RuCl}_2(\text{dppe})_2]$ and NaOTf by a procedure similar to that for reported for $[\text{RuCl}(\text{dppe})_2]\text{PF}_6$.^[14a] A solution of NaOTf (11.3 g, 12.4 mmol) and *cis*- $[\text{RuCl}_2(\text{dppe})_2]$ (10.0 g, 10.3 mmol) in THF (100 mL) and EtOH (50 mL) was stirred at room temperature for 12 h under 1 atm of Ar. After evaporation of the solvents, the residue was extracted with CH_2Cl_2 (20 mL). Addition of hexane to the concentrated solution gave $2 \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$ (8.96 g, 7.97 mmol, 77%) as dark red crystals; $^1\text{H NMR}$ (CDCl_3): $\delta = 1.65$ (br. s, 4H), 2.56 (br. s, 2H), 2.65 (br. s, 2H), 6.78–7.76 (m, 40H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 55.6$ (br. t, $J = 12$ Hz), 83.7 (br. t, $J = 12$ Hz); elemental analysis (%) calcd for $\text{C}_{53}\text{H}_{48}\text{ClF}_3\text{O}_3\text{P}_4\text{SRu} \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$: C 57.12, H 4.39; found: C 57.13, H 4.57.

7: To a solution of **8** (1.152 g, 0.83 mmol) in dichloromethane (10 mL) and THF (10 mL) was added HOTf (80 μL) by syringe under 1 atm of H_2 . The reaction mixture was stirred at room temperature for 30 min. The color of the solution turned from yellow to red during the reaction. Hexane (50 mL) was then added to the reaction mixture to give a pale red solid **7**, which was collected by filtration, washed with hexane (3×20 mL), and dried under reduced pressure (1.050 g, 0.68 mmol, 82%); $^1\text{H NMR}$ (CD_2Cl_2): $\delta = -9.11$ (br., 2H), 5.2–8.8 (m, 64H); a minimum T_1 value of 21 ms (400 HMz) at 243 K was obtained for the broad signal at $\delta = -9.11$, assignable to $\eta^2\text{-H}_2$; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 2.5$ (t, $J = 27$ Hz), 26.3 (t, $J = 27$ Hz); elemental analysis (%) calcd for $\text{C}_{89}\text{H}_{66}\text{ClF}_3\text{O}_3\text{P}_4\text{SRu}$: C 69.73, H 4.34; found: C 69.74, H 4.38.

Asymmetric protonation of **6c with **7** (Scheme 6):** A solution of **6c** was prepared by lithiation of **1c** (25.0 mg, 0.10 mmol) with methylolithium (0.10 mL of 1.02 N solution in diethyl ether, 0.10 mmol) in Et_2O (3 mL) at room temperature for 2 h under 1 atm of N_2 . A solution of complex **7** (150 mg, 0.10 mmol) in dry dichloromethane (5 mL) was then added to the above solution of **6c** at -78°C under 1 atm of H_2 . The mixture was stirred at that temperature for 4 h under 1 atm of H_2 . Then the reaction mixture was gradually warmed up to room temperature and stirred at room temperature for 12 h. GLC analysis showed the formation of **3c** (>95%). The solvent was removed under reduced pressure, and the residue was extracted with Et_2O (3×5 mL). The extract was purified by TLC (SiO_2 , hexane/ $\text{EtOAc} = 7/3$ as eluent) to afford **3c** as a pale yellow liquid (12 mg, 0.075 mmol, 75%). The remaining residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give **8** as a yellow solid (95 mg, 0.069 mmol, 69%). The absolute configuration of (*S*)-**3c** was determined by its optical rotation; $[\alpha]_D^{25} = -30$ ($c = 0.40$ in dioxane); the 75% ee value of (*S*)-**3c** was determined by GLC (helium carrier gas, 120 $^\circ\text{C}$ column temperature, 20:1 split ratio) on a cyclodextrin phase (Chiraldex GT-A, 30 m); retention time of (*R*)-**3c** = 22.87 min (12.6%); retention time of (*S*)-**3c** = 24.01 min (87.4%).

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- [11] In the catalytic hydrogenation of trimethylsilyl enol ethers, the corresponding ketones are sometimes observed as by-products. This is explained by the reaction of trimethylsilyl enol ethers with adventitious water in the solvent.
- [12] Since no enantioselectivity was observed in the stoichiometric reaction of **1c** (see Scheme 2) with **7** (see Scheme 6), we consider that the hydrogenolysis of trimethylsilyl enol ethers catalyzed by **4** (see Scheme 4) proceeds through O-protonation by the activated H_2 ligand.^[13] Thus, in this novel reaction an enol product is initially produced, which isomerizes to the corresponding keto form.
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